

**SURFACE CHEMICAL STUDIES OF "HOT CORROSION LIFE PREDICTION MODEL
FOR MARINE GAS TURBINE BLADES AND GUIDE VANES"**

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ABSTRACT

The results of a theoretical program of research directed towards the study of hot corrosion in the hot gas pathways of marine gas turbines burning vanadium contaminated liquid fuels are presented here. A life prediction model, Life, is developed for turbine blades and guide vanes based on the application of fundamental heat, mass, and momentum transfer principles to the chemically reactive non-isothermal combustion environment. The corrosion rate is assumed to be limited by high Schmidt number diffusional dissolution of a protective oxide species into the condensed molten salt solution (equilibrium composition is predicted by means of free energy minimization by the computer program). Alloy surface effects are included to quantitatively relate predicted coating removal rate to hot corrosion data which are used to verify the validity of our theoretical approach. The physical insight into the mechanism of hot corrosion obtained through the study is expected to provide far reaching implications for the future design and protection of marine turbine components.

INTRODUCTION

Fuel composition, among other things, controls the corrosion and hence the life of airfoil material in the marine gas turbine engine. The use of fuels containing contaminants like sulfur, sodium, vanadium and sea salts, is known to cause rapid degradation of alloy coatings as well as substrate alloys of the blades and vanes. Molten salt mixtures of sulfates, vanadates and other hot corrosive species such as oxides of vanadium and sulfur formed as fuel combustion products dissolve the protective oxide on the blade surface. During fluxing a variety of complex chemical reactions take place which required analysis by computer-based multicomponent equilibrium algorithms. The high-Schmidt number Brownian diffusion limited oxide dissolution by the deposited liquid has been assumed to be the rate-limiting process in hot corrosion. Each of these processes has been characterized thoroughly and rigorously. The corrosion rate increases with the salt deposition rate, but the relationship is nonlinear and depends on the composition of the salt and the

substrate alloy or coating. Sodium as a fuel impurity or as airborne sea salts in the marine atmosphere condenses as sodium sulfate (Na_2SO_4) and causes corrosion. In the temperature range 600-800°C, low temperature, hot corrosion is very sensitive to SO_2 partial pressures in the gas phase. In the range 800-950°C, high temperature, hot corrosion is not quite as sensitive to SO_2 levels. A theoretical model (1,2) for hot corrosion limited blade life based on the rates at which oxide formation and dissolution phenomena proceed, has been developed from theoretical considerations by the use of computer programs (3,4,5). The predictive computer program is called Life. The predicted effect of variations in operating parameters and surface coating oxides on predicted blade life has been studied.

Blade surfaces are usually coated with metal alloys that form an adherent, refractory and corrosion-resistant oxide layer on the gas side of the coating. Rosner and Nagarajan (6) have proposed the following mechanism for initiation and propagation of hot corrosion: at locations where the protective oxide scale is partially leached or completely dissolved by the condensed molten salt-'solvent', the metal substrate is more accessible, and hence vulnerable to catastrophic corrosion. Local saturation of the liquid layer is prevented by dynamic fluxing due to aerodynamic and centrifugal-shear forces which convey dissolved oxide from the site of dissolution to the tip and trailing-edge regions of the blade. The oxide dissolution rate is taken to be limited by high-Schmidt number Brownian diffusion of the oxide species in the melt (as well as by salt/oxide interfacial detachment kinetics). Other parameters that play a role in the oxide dissolution rate include aerodynamic variables such as the convective flux of the gas phase alkali contaminants, and material integrity characteristics of the blade alloy surface.

Many studies have been concerned in the literature with deposition mechanisms, the composition of the salt deposits (7) and mechanisms of low temperature hot corrosion (8). But our model for predicting the life of air foils, is based on fundamental principles. Objective of the present work is to understand the interfacial chemistry of the deposition and corrosion processes approach.

STEPS IN THE ANALYSIS

1. Equilibrium thermodynamic prediction of condensed liquid and vapor phase compositions (3).
2. Chemically Frozen Boundary Layer (CFBL) model prediction of deposition rates (4,5).
3. Estimation of physico-chemical properties of the molten salt solution.
4. Estimation of physical properties and parabolic oxidation rate constants of coating alloys.
5. Prediction of protective oxide coating dissolution rates into the condensed liquid 'solvent'.
6. Prediction of blade 'life' based on the competing dynamics of

oxide layer formation and dissolution.

Each of these steps, along with the assumptions inherent in each was previously addressed (1).

RESULTS AND DISCUSSION

High temperature hot corrosion mechanisms reported in literature (7,8) are not based on rate studies. Model reported in this paper is a rate study model and it uses the multicomponent chemical vapor deposition (CVD) theory (9,10).

Local thermochemical equilibrium calculations by use of solution capable free energy minimization computer programs i.e., Complex Chemical Equilibria Calculations (CEC) of the National Aeronautics and Space Administration (NASA) and Package code of the Department of Energy (DOE) are shown in figures 1 and 2. Mole fractions of the product species depend upon the impurity concentrations in the fuels (table 1).

Figure 1. CEC predicted dominant vapor species.

Figure 2. Condensed liquid solution comprising principally of $\text{Na}_2\text{SO}_4(l)$, $\text{Na}_2\text{V}_2\text{O}_6(l)$, and $\text{V}_2\text{O}_5(l)$.

Figure 3. Shows dependence of the CFBL computed deposition rate on surface temperature and fuel/air ratio.

At sufficiently low surface temperatures, the solution deposition rate is insensitive to surface temperature. As the solution dew point is approached, deposition rate drops to zero at the dew point. The dew point of the solution is in general, higher than that for any of the individual species. This dew point elevation effect, in combination with the freezing point depression effect and eutectic formation, considerably broaden the unsafe temperature range in which the deposit remains molten. For this reason, solution condensates are typically corrosive over a wider operating regime than pure condensates.

Molten salt deposition rate increases with an increasing fuel-to-air ratio, increasing gas main stream temperature, and with increasing sodium/vanadium concentrations in the combustion mixture. Pressure and sulfur level are predicted to have relatively insignificant effects on the computed deposition rate.

Figure 4. Shows dependence of oxide dissolution rate on blade surface temperature. Oxide dissolution rate can actually increase with temperature, even though the salt deposition rate drops rapidly. Oxide dissolution rate is predicted to increase with increasing fuel-to-air ratio, increasing gas mainstream temperature, and increasing sodium/vanadium gas phase concentrations. The rate as with deposition is insensitive to

pressure and sulfur level under normal turbine operating conditions.

Figure 5. Shows for pure metallic oxide coated turbine blades there is a monotonic increase in blade life with temperature since sulfidation corrosion only is considered as the life limiting factor. This inconsistency is due to omission of oxidation corrosion as also life limiting.

Figure 6. Predicts maximum blade life at the temperature when the sulfidation corrosion and oxidation corrosion intersect approximately at 1120K.

Figure 7. Shows evaluation of three Navy test fuels with regard to their corrosion potential. Below 1200 K, use of GT 10 would result in longer blade life than GT 12. NSFO (Navy special fuel oil) is a highly contaminated fuel not used in gas turbine engine.

Figures 8 and 9. Show life of blade material coated with several single metal oxides mostly.

Figure 10. Shows life of blade coated with typical metallic alloys and dependence of life on temperature.

CONCLUSIONS

Objective, central to the preliminary approach was accomplished. There is reasonable agreement between the model predictions and some of the experimental results reported in literature (11). The model needs improvement. Thermodynamic data on vanadium-oxygen gaseous species is lacking (12) in the thermodynamic data base (13,14). Ideal solution calculations are to be replaced by real solution calculations using the SAGE program which is a modified and improved version of sol-gas-mix program.

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Table 1. Impurity concentrations in three Navy test fuels.

Impurity	Fuel		
	GT 10	GT 12	NSFO
Sodium (wt. ppm)	1	2	22
Vanadium (wt. ppm)	—	5	170
Sulfur (wt. %)	1	2	2
Nickel (wt. ppm)	—	—	34
Zinc (wt. ppm)	—	—	2
Iron (wt. ppm)	—	—	11

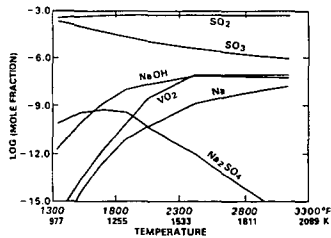


Fig. 1. CEC-predicted vapor phase composition, fuel GT 12, pressure = 1 atmosphere, fuel/air = 1/30.

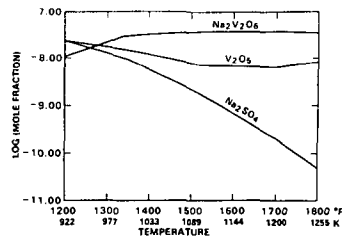


Fig. 2. CEC-predicted liquid phase composition, fuel GT 12, pressure = 1 atmosphere, fuel/air = 1/30.

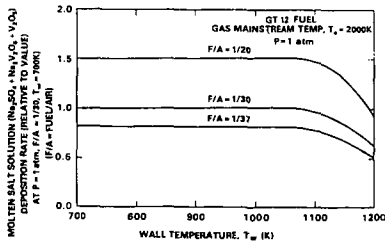


Fig. 3. CFBL deposition rate calculations: predicted dependence on fuel/air (F/A) ratio and blade surface temperature T_w (°K).

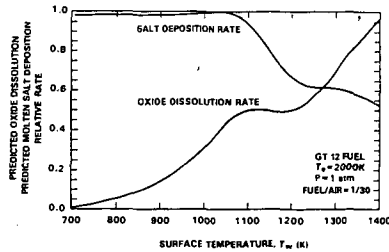


Fig. 4. Predicted effect of blade surface temperature on molten salt deposition and relative oxide (RO) dissolution rates.

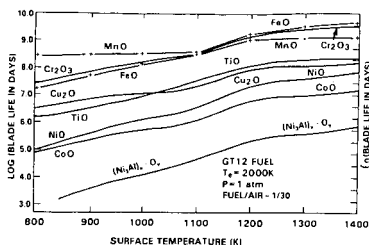


Fig. 5. Predicted hot corrosion-limited life of oxide-coated turbine blades; effect of surface temperature changes.

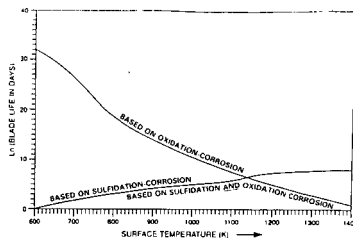


Fig. 6. Predicted surface temperature dependence of Cr_2O_3 -coated blade limited by sulfidation, oxidation, and a combination of the two; fuel GT 12, $T_g = 2,000$ K, $P = 1$ atm, $\mu_{fuel/air} = 0.0333$.

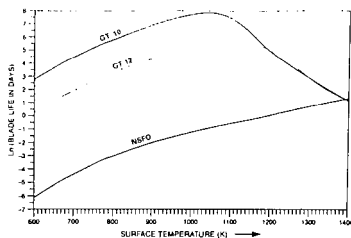


Fig. 7. Evaluation of three heavy test fuels with respect to their corrosion potential; protective coating Cr_2O_3 , fuels GT 10, GT 12, NSFO, $T_g = 2,000$ K, $P = 1$ atmosphere, $\mu_{fuel/air} = 0.0333$.

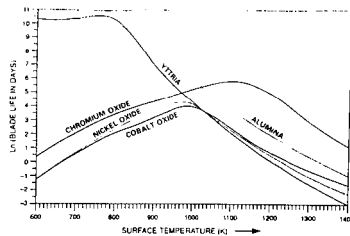


Fig. 8. Computed surface temperature dependence of corrosion-limited life of blades coated with several pure metallic oxides; fuel GT 12, $T_g = 2,000$ K, $P = 1$ atmosphere, $\mu_{fuel/air} = 0.0333$.

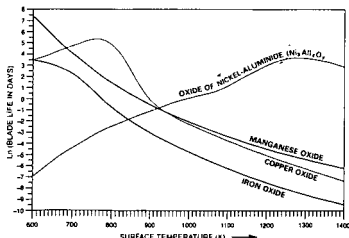


Fig. 9. Predicted surface temperature dependence of corrosion-limited life of blades coated with several metallic and alloy oxides; fuel GT 12, $T_g = 2,000$ K, $P = 1$ atmosphere, $\mu_{fuel/air} = 0.0333$.

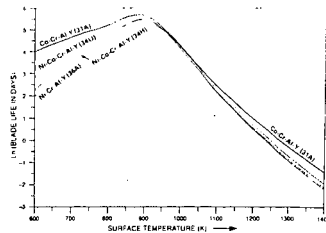


Fig. 10. Predicted surface temperature dependence of corrosion-limited life of blades coated with typical protective alloys; fuel GT 12, $T_g = 2,000$ K, $P = 1$ atmosphere, $\mu_{fuel/air} = 0.0333$.